

**Center for Catalytic Hydrocarbon Functionalization**  
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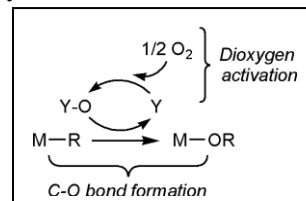
*Mission Statement:* The CCHF fosters collaborations between groups with expertise in catalysis, electrochemistry, bioinorganic chemistry, materials chemistry and quantum mechanics to enable fundamental advancements in the design and development of next generation catalysts for selective, low temperature, hydrocarbon functionalization.

Catalysts are central to the efficient and clean utilization of energy resources, and they impact all aspects of the energy sector. Catalysts: a) mediate the transformation of hydrocarbon raw materials into forms that are useful to the materials, chemistry, power and transportation industries, b) reduce energy consumption and waste production for large scale commodity processes, and c) convert harmful by-products (*e.g.*, by-products of combustion) into more environmentally benign forms. Consequently, catalysis is a cornerstone of the chemical industry; however, maintaining a steady and clean supply of energy to the developing global population and accessing new energy resources will require dramatic advancements in the catalysis arena. A central tenet of the Center for Catalytic Hydrocarbon Functionalization (CCHF) is that the development of advanced catalysts that allow controlled and selective conversion of C-H bonds to C-O and C-C bonds are key to more efficient use of fossil resources as well as future use of solar energy and biomass.

Fossil raw materials, which provide almost all of our energy, are primarily hydrocarbons (molecules that contain only carbon and hydrogen). Unfortunately, the current high temperature processes that convert these raw materials lead to low efficiency, high costs, excessive emissions (including carbon dioxide) and a disproportionate dependence on imported petroleum. In the near term, the increased worldwide demand for energy will be impossible to sustain without dramatic developments that lead to new technologies that optimize the utilization of fossil resources. For example, increasing the rate and selectivity for the transformation of C-H bonds in reactions with oxygen is central to new catalysts that substantially enhance energy efficiency, reduce emissions, increase use of *domestic* resources (*e.g.*, methane from natural gas), and convert carbon dioxide into more environmentally benign forms. The CCHF brings together a broad based collaborative team with the expertise to accelerate advances in fundamental aspects of catalyst technologies required for selective hydrocarbon functionalization. These efforts can have broad impact vis-à-vis increasing domestic energy sources, mitigating negative impact on the environment and providing tools for utilization of biomass and solar energy.

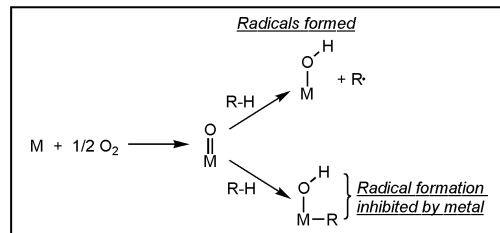
The development of efficient catalysts for the conversion of hydrocarbons into higher value materials (*e.g.*, the conversion of methane to liquid fuels such as methanol) requires novel systems based on *new chemical transformations*. In order to transform hydrocarbons, the catalysts must: a) break at least one C-H bond, b) mediate the formation of a new bond of carbon with a heteroatom {*e.g.*, alcohol production ( $R-H \rightarrow R-OH$ ) requires a new carbon-oxygen bond}, and c) release the functionalized product with protection against additional reaction. In order to provide the new science needed to enable chemists to design such smart catalysts, the CCHF will focus on three initial "thrust" areas:

**1. New Methods for Carbon-Heteroatom Bond Formation:** A primary focus of the CCHF is the controlled (and potentially reversible) conversion of hydrocarbons to "functionalized" materials (*e.g.*, oxygenated compounds such as alcohols). The formation of carbon-heteroatom bonds, one step in overall hydrocarbon functionalization, is a major chemical challenge. For example, reactivity of metal hydrocarbyl complexes (metals with alkyl or aryl ligands) with oxidants to deliver a new C-O bond has been a vexing challenge for this field, and particularly difficult is finding a method to incorporate dioxygen as the oxygen atom source. On the other hand, enzymatic systems routinely use dioxygen to deliver oxygen atoms to hydrocarbons and related compounds. The PIs in the CCHF will pool insight from



complementary backgrounds, including bioinorganic, organometallic, electrochemistry and computational chemistry, to develop new pathways for these transformations and to garner a new atomic level understanding of how the features of the metal work in concert with the oxidant to promote the reactions. We will focus on the design of new classes of organometallic complexes that react readily with oxygen sources, new methods to activate dioxygen into forms that can deliver oxygen atoms, new technologies that permit controlled and reversible C-O bond formation, and computational methods capable of predicting accurately the best materials on which to focus the experiments.

**2. New Classes of Metal Oxo Complexes:** Nature functionalizes hydrocarbons using metal-oxo complexes (*i.e.*, systems with M=O bonds) in which the metal is in a high oxidation state (*i.e.*, the metal is electron deficient). The ability of chemists to replicate the reactivity of these enzymes using synthetic models is limited. By combining expertise in bioinorganic chemistry, homogeneous and heterogeneous catalysis, and computational chemistry the CCHF will pursue new strategies to synthesize metal oxo systems that provide more controlled hydrocarbon functionalization chemistry. For example, one pursuit will be the design of systems with new electronic structures that are less amenable toward radical reactivity (odd-electron transformations), which generally decreases selectivity thereby decreasing catalyst efficiency. Designing systems that can activate dioxygen, while avoiding radicals, and selectively functionalize hydrocarbons requires significant advances that can only be achieved by combining computational chemistry, organometallic catalysis and bioinorganic themes.



**3. Developing new "environments" for hydrocarbon chemistry:** A substantial challenge for selective hydrocarbon functionalization, especially partial oxidation, is developing catalytic systems that can react with inert hydrocarbons but that are inhibited toward reaction with the functionalized products, which are almost always more reactive than the starting hydrocarbon feedstock. Most previous work to solve this problem has focused on homogeneous catalysts, since such systems are usually more amenable to tuning of reactivity toward specific substrate selectivity than heterogeneous catalysts. Groups in the CCHF will initiate new avenues for such reactions by designing advanced materials to control reaction environments. These collaborations between molecular and materials chemists will seek catalysts at the nanoscale that provide new modes of selectivity for reactivity with hydrocarbons while limiting reactivity with functionalized products.

**Summary:** We have mounted collaborative efforts on three parallel developments most likely to provide the new understanding needed for rationale development of novel materials for controlled hydrocarbon functionalization.

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